

SPACE DURABLE POLYIMIDE/CARBON NANOTUBE COMPOSITE FILMS FOR ELECTROSTATIC CHARGE MITIGATION

Kent A. Watson,* Joseph G. Smith, Jr. and John W. Connell
National Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23681-2199

ABSTRACT

Low color, space environmentally durable polymeric films with sufficient electrical conductivity to mitigate electrostatic charge (ESC) build-up have been under investigation as part of a materials development activity. These materials have potential applications on advanced spacecraft, particularly on large, deployable, ultra-light weight Gossamer spacecraft. The approach taken to impart sufficient electrical conductivity into the polymer film is based on the use of single walled carbon nanotubes (SWNT) as conductive additives. Earlier approaches investigated in our lab involved both an in-situ polymerization approach and addition of SWNT to an oligomer containing reactive end-groups as methods to improve SWNT dispersion. The work described herein is based on the spray coating of a SWNT/solvent dispersion onto the film surface. Two types of polyimides were investigated, one with reactive end groups that can lead to bond formation between the oligomer chain and the SWNT surface and those without reactive end-groups. Surface conductivities (measured as surface resistance) in the range sufficient for ESC mitigation were achieved with minimal effects on the mechanical, optical, thermo-optical properties of the film as compared to the other methods. The chemistry and physical properties of these nanocomposites will be discussed.

KEY WORDS: Low Color Polyimides, Polyimides, Nanocomposites, Electrostatic Charge Mitigation, Carbon Nanotubes, Space Durable Polyimides

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1. INTRODUCTION

Large, deployable, ultra-light weight (e.g. Gossamer) spacecraft will require film-based polymeric materials that possess a unique combination of mechanical, optical, and thermo-optical properties (1). These requirements depend on the intended mission and accordingly orbital environment of the spacecraft. Some of the desired properties include atomic oxygen (AO) resistance [for spacecraft in low Earth orbit (LEO)], low solar absorptivity (low color), high thermal emissivity, resistance to ultraviolet (UV) and vacuum UV radiation, good mechanical properties, good processability and handling, toughness, tear resistance, ability to be folded and unfolded and sufficient electrical conductivity for dissipation of electrostatic charge (ESC) buildup. The overall goal of this work is to prepare transparent, flexible, anti-static, space environmentally durable polymer films for use on future NASA missions.

Many of the properties required for these applications are realized with aromatic polyimides due to their exceptional physical and mechanical properties as well as resistance to UV and charged particle radiation. By the proper choice of the monomers, low color (low solar absorptivity) and atomic oxygen resistance polyimides have been prepared (2,3). However, the incorporation of sufficient electrical conductivity to mitigate ESC build-up without detracting from the other desired properties, particularly low color and flexibility, has been difficult to attain. Intrinsic electrical conductivity is needed due to the charged orbital environment. Insulating materials that are exposed to this environment become charged and can behave like a capacitor. The problem occurs when the material discharges. This can occur in a single event that can cause damage to surrounding materials and electronics on the spacecraft. The surface resistance that is needed to mitigate ESC buildup is in the range of 10^6 to 10^{10} ohms/square.

One approach to imparting conductivity into these films without severely detracting from the desired optical and thermo-optical properties is through the use of single walled carbon nanotubes (SWNTs). Discovered in the early 1990s (4,5), SWNTs have shown great potential for improving primarily the electrical properties of materials. Achieving good dispersion of SWNTs throughout the polymer matrix has been difficult due to the insolubility of the material and/or incompatibility with the host resin. Typically, CNTs tend to agglomerate as bundles in solvents and the host resin and if dispersed, can re-agglomerate soon thereafter due to electrostatic attraction when agitation is removed.

Reasonable dispersions of SWNTs in some space environmentally durable polymers have been reported (6-8). This was achieved by using both an in-situ polymerization approach and the addition of SWNTs to amide acid oligomers containing reactive groups. The first method involved the preparation of the amide acid in the presence of the SWNTs with simultaneous ultrasonic treatment followed by thermal conversion to the polyimide. Alternatively, the amide acid/SWNT mixture can be cyclodehydrated chemically in solution provided that the polyimide

remains soluble. The second approach involved the dispersion of SWNTs in solutions of alkoxysilane terminated amide acid oligomers (9). Alkoxysilane containing materials, typically referred to as coupling agents, are known to aid in the adhesion of organic materials to substrates such as glasses, metals, ceramics, and potentially SWNTs through reaction with hydroxyl functionalities present on the surface. Oxygenated species such as carboxylic acid and hydroxyl groups are formed on SWNT ends as a result of certain purification methods involving strong oxidizing acids (10). In this approach, it was anticipated that the alkoxysilane functional ends on the oligomer, once hydrolyzed, would condense with functionalities present on the ends of the purified SWNTs. In both of these approaches, the SWNTs were dispersed throughout the polymer matrix and consequently the nanocomposite films exhibited similar surface and volume resistivities. In cases with the SWNT loading level above 0.05 weight percent, surface and volume resistivities sufficient for ESC mitigation were achieved. However, there was notable loss of the optical transparency and an increase in the solar absorptivity as compared to the host polymer.

Many applications for polymers on space vehicles require sufficient surface conductivity to mitigate ESC and volume conductivity is not necessary. For these cases, the coating of SWNTs on one side of the polymer film was investigated. The amount of SWNTs necessary for ESC buildup is greatly reduced when only surface conductivity is required as compared to films containing SWNTs dispersed throughout. The use of a lower amount of SWNTs would be expected to have less of an effect on the optical and thermo-optical properties. The preparation and characterization of nanocomposite films derived from a space durable polyimide (LaRCTM CP2) and SWNTs applied through a spray-coating method is described herein.

2. EXPERIMENTAL

2.1 Starting Materials Aminophenyltrimethoxysilane (APTS, Gelest Inc., 90% meta, 10% para) and 1,3-bis(3-aminophenoxy)benzene [APB, Mitsui Chemicals America, Inc. melting point (m.p.) 107-108.5 °C] were used without further purification. 4,4'-Hexafluoroisopropylidene diphthalic anhydride (6FDA, Hoechst Celanese Inc., m.p. 241-243 °C) was sublimed prior to use. HiPCO SWNTs were obtained from Tubes@Rice. The SWNTs were purified by soxhlet extraction with hydrochloric acid for ~24 hours, then treated at 250 °C for 8 hours in a high humidity chamber. All other chemicals were used as received without further purification.

2.2 Polymer Synthesis APB (6.7470 g, 0.0231 mol) and N,N-dimethylacetamide (DMAc, 30.0 mL) were placed into a 250 mL three neck round-bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube filled with calcium sulfate. Once dissolved, 6FDA (10.3044 g, 0.0232 mole, 0.5% offset) was added with additional DMAc (38.2 mL) to afford a solution with a solids content of 20% (w/w). The solution was stirred overnight at ambient temperature under a nitrogen atmosphere. The remaining polymer solution was chemically

imidized (e.g. cyclodehydrated) by the addition of 7.1 g of acetic anhydride and 5.5 g of pyridine and stirring at ambient temperature overnight. The polymer was precipitated in a blender containing water, filtered, washed with excess water and dried in a vacuum oven at 110 °C overnight to afford a white, fibrous material.

2.3 Synthesis of Oligomers The alkoxy silane terminated amide acids (ASTAAs) were prepared by the reaction of 6FDA with APB and end-capped with APTS at a 2.5% molar offset. The calculated number average molecular weight (M_n) was ~27,700 g/mole. The oligomer was prepared by dissolving APB (4.9522 g, 0.0169 mol) and APTS (0.1853 g, 0.0009 mol) in DMAc (7 mL) in a three neck round-bottomed flask equipped with a mechanical stirrer, thermometer and nitrogen gas inlet and outlet. The flask was then immersed in a water bath to regulate the temperature. 6FDA (7.7184 g, 0.0174 mol) was added in one portion as a slurry in DMAc (10 mL) and rinsed in with 9 mL of DMAc to afford a solution with a solid content of ~34.4% (w/w). The reaction was stirred for ~24 hours at ambient temperature under nitrogen. An aliquot was removed to determine inherent viscosity. For film casting, the solution was diluted with an additional 21 mL DMAc to afford a solids content of ~22.5% (w/w).

2.4 Films Solutions of LaRC™ CP2 in N,N-dimethylformamide (DMF) were doctored onto clean, dry plate glass and dried to tack-free state in a low humidity chamber at ambient temperature. The films were then spray-coated with SWNTs as described in section 2.5. The SWNT spray-coated films were dried in a forced air oven and staged to 250 °C for 1 hr. DMAc solutions of the ASTAAs (as described in section 2.3) were doctored onto clean, dry plate glass and dried to tack-free state in a low humidity chamber at ambient temperature. The films were then spray-coated with SWNTs as described in section 2.5. The SWNT spray-coated films were cured in a forced air oven at 100, 200, and 300 °C for 1 hour each. The films were subsequently removed from the glass plate and characterized.

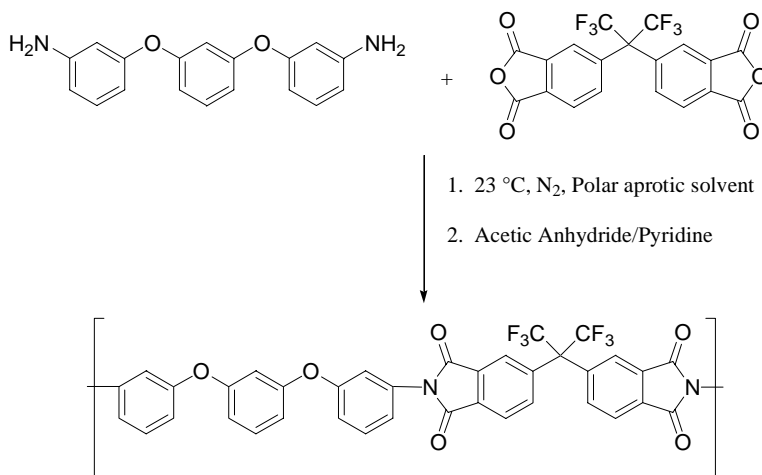
2.5 Spray Coating of SWNT A SWNT/DMF mixture was prepared by placing 0.0020 g of purified SWNTs in 10.00 g DMF. The mixture was placed in an ultrasonic bath operating at 40 MHz for 16 to 24 hrs. An airbrush (Badger Model 250) was used to apply the SWNT/DMF suspension to the tack-free films.

2.6 Other Characterization Inherent viscosities were obtained on 0.5% (w/v) amide acid solutions in DMAc at 25 °C. Melting point ranges (tangent of onset to melt and the endothermic peak) were determined by either DSC at a heating rate of 10 °C/min or visually on a Thomas-Hoover capillary melting point apparatus (uncorrected). The % transmission at 500 nm was obtained on thin films using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. Solar absorptivity (α) was measured on an AZ Technology Model LPSR-300 spectrophotometer with measurements taken between 250 to 2800 nm using a vapor deposited aluminum on Kapton® film (1st surface mirror) as a reflective reference for air mass 0 per ASTM E903. An

AZ Technology Temp 2000A infrared reflectometer was used to measure thermal emissivity (ϵ). Surface resistivity was measured using a Prostat® PSI-870 Surface Resistance and Resistivity Indicator per ASTM D-257 and was reported as an average of 3 readings.

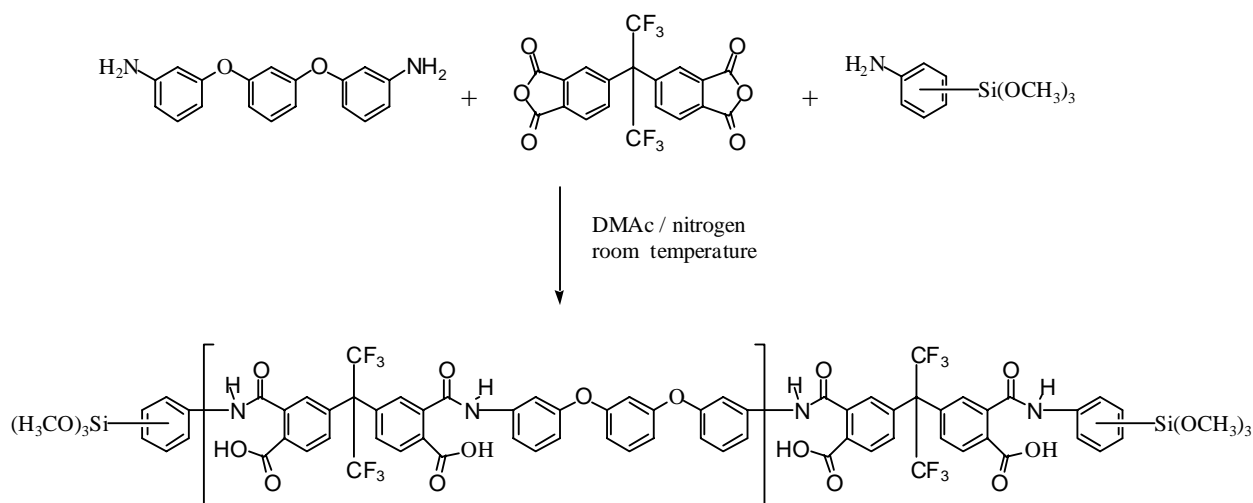
3. RESULTS AND DISCUSSION

3.1 LaRC™ CP2 Synthesis In this study, LaRC™ CP2, a low color space durable polymer, was prepared with and without alkoxy silane end-caps. The unend-capped polymer was prepared by the traditional amide acid route as depicted in Scheme 1. The intermediate poly(amide acid) solution had an inherent viscosity of 1.07 dL/g. Imidization (e.g. cyclodehydration) was conducted in solution by the addition of a solution of pyridine and acetic anhydride. The resultant polyimide was isolated as a white fibrous solid with an inherent viscosity of 0.98 dL/g. The polyimide was dissolved in DMF to cast thin films that were subsequently spray-coated with a SWNT dispersion.



Scheme 1. LaRC™ CP2 Synthesis

The alkoxy silane terminated amide acid (ASTAA) was prepared at a 2.5% molar offset corresponding to a calculated \overline{M}_n of ~27,700 g/mol as illustrated in Scheme 2 (9). As with traditional amide acid synthesis, the diamine and amine containing end-cap were initially dissolved in DMAc. The dianhydride was then added to the stirred solution. To prevent a temperature increase due to the heat of reaction and prevent premature reaction of the alkoxy silane groups, the flask was immersed in a water bath at room temperature. The ASTAA mixture was stirred overnight at room temperature under a nitrogen atmosphere. The inherent viscosity of the ASTAA was 0.73 dL/g. This solution was used to cast thin films that were subsequently spray coated with a SWNT dispersion.



Scheme 2. Alkoxysilane-Terminated Amide Acid of LaRC™ CP2 Synthesis

3.2 Spray-Coating SWNT onto Polyimide Films To date, sufficient surface resistivity for ESC mitigation has been obtained by dispersing the SWNT throughout the bulk of the polymer film. By this approach, the loading level needed to attain conductivity has led to darkening of the films with concurrent decreases in the optical and thermo-optical properties of the nanocomposite as compared to the virgin material. These nanocomposite films exhibited similar levels of both surface and volume conductivity.

Many applications on advanced spacecraft require conductivity on only one surface of the film. One approach to impart sufficient conductivity to one surface for ESC mitigation is by spray-coating the film with SWNTs. Typically a homogeneous solution is used in spray-coating processes; however, dispersions of the SWNTs in DMF were found to work well due to the size of the SWNT. After several trials, the best results were obtained using films that were dried to a tack-free state at room temperature (e.g. still contain significant amounts of solvent). Films that had been fully dried/cured exhibited areas of SWNT aggregation and poor wetting characteristics. Additionally it was observed that several light coats with drying to a tack-free state in a low humidity chamber at room temperature in between coats provided the best dispersions of SWNTs on the film surface. As with spray painting, heavy spray coats led to pooling and running of the solution on the film surface, ultimately leading to SWNT re-aggregation. This was due to the solvent surface tension and low solids content of the solution in conjunction with the electrostatic forces allowing the SWNTs to re-agglomerate into larger bundles.

3.3 Optical Transparency Thin films were measured for optical transparency at 500 nm, the solar maximum, with the results presented in Table 1. In general, the optical transparency of the spray-coated films was slightly lowered due to the presence of SWNTs as compared to the virgin

material (P2 and P3 as compared to P1 and P8 and P9 as compared to P4). Spray-coated film P10 exhibited a marked decrease in optical transmission and was due to multiple coatings of the film with the SWNT/DMF mixture. However, due to differences in film thickness true comparisons between the spray-coated samples and the virgin material can't be made. Based on internal work though, differences in film thickness within these ranges for the pristine samples (films not containing SWNT dispersed or as a coating) had a negligible effect upon the optical properties of the virgin material.

A comparison of films containing SWNTs mixed throughout the bulk of the film at several loading levels (P5-P7) and with films containing SWNTs coated only on the surface (P8-P10) is shown in Table 1. As expected, the spray-coated films (P8 and P9) exhibited better retention of optical transmission as compared to the virgin sample (P4) than the films where the SWNT were dispersed throughout the matrix (P5-P7). Spray-coated film P10 exhibited comparable optical transmission as P5 due to the reasons stated above. The % transmission of the spray coated films ranged from 68 to 83 with no relationship to thickness observed. The spray coating method is new and not optimized with many variables associated with it thus accounting for some of the differences observed.

Table 1. Optical Transparency at 500 nm

ID	Description	Film Thickness, μm	Transmission, %
P1	LaRC TM CP2	13	89
P2	SWNT Spray-Coated LaRC TM CP2	28	83
P3	SWNT Spray-Coated LaRC TM CP2	38	72
P4*	ASTAA LaRC TM CP2	38	86
P5*	ASTAA LaRC TM CP2 with 0.03 % (w/w) SWNT	38	67
P6*	ASTAA LaRC TM CP2 with 0.05 % (w/w) SWNT	41	59
P7*	ASTAA LaRC TM CP2 with 0.08 % (w/w) SWNT	38	53
P8	SWNT Spray-Coated ASTAA LaRC TM CP2	50	79
P9	SWNT Spray-Coated ASTAA LaRC TM CP2	30	81
P10	SWNT Spray-Coated ASTAA LaRC TM CP2	32.5	68

* Reference 9

3.4 Thermo-optical Properties of Nanocomposites The effect of SWNT spray-coating on the solar absorptivity (α) and thermal emissivity (ϵ) was of interest since these properties are important for some applications on Gossamer spacecraft. Solar absorptivity (α) pertains to the fraction of incoming solar energy that is absorbed by the film and is typically low (~ 0.1) for a low color film. The thermal emissivity (ϵ) is a measure of the films ability to radiate energy from the film surface. Solar absorptivities of films coated with SWNTs were compared to films cast from polymers that were prepared in the presence of SWNTs (P5-P7) (10). Results of this comparison are shown in Table 2. In general, the spray coated films exhibited lower α s than the films where the SWNTs were dispersed throughout the bulk as expected. This is related to an effective concentration of SWNT present in the light path which is reflected in the results. Films prepared from P5, P6 and P7 contain SWNTs throughout the bulk of the film. In general, the SWNT spray-coated films based on the ASTAA LaRC™ CP2 (P8-P10) exhibited solar absorptivities less than the films containing SWNT loaded throughout the bulk of the film (e.g., P6). However, a direct comparison can't be made due to differences in film thickness between

Table 2. Thermo-optical Properties

ID	Description	Film Thickness, μm	Solar Absorptivity, α	Thermal Emissivity, ϵ
P1	LaRC™ CP2	13	0.07	0.57
P2	SWNT Spray-Coated LaRC™ CP2	28	0.09	0.54
P3	SWNT Spray-Coated LaRC™ CP2	38	0.21	0.52
P4*	ASTAA LaRC™ CP2	38	0.07	0.59
P5*	ASTAA LaRC™ CP2 with 0.03 % (w/w) SWNT	38	0.21	0.63
P6*	ASTAA LaRC™ CP2 with 0.05 % (w/w) SWNT	41	0.30	0.65
P7*	ASTAA LaRC™ CP2 with 0.08 % (w/w) SWNT	38	0.35	0.67
P8	SWNT Spray-Coated ASTAA LaRC™ CP2	50	0.13	0.67
P9	SWNT Spray-Coated ASTAA LaRC™ CP2	30	0.12	0.52
P10	SWNT Spray-Coated ASTAA LaRC™ CP2	32.5	0.20	0.56

*Reference 9

the samples. Films P9 and P10 gave ϵ values that were less than the pristine sample. It was unexpected that the thermal emissivity of P8 was comparable to that of P7 even though it exhibited a low α .

3.5 Surface Resistivity The conductivity of the films was determined as surface resistivity under ambient conditions with the results presented in Table 3. It was observed that the spray-coated films (P2, P3 and P8-P10) exhibited surface resistivities that were acceptable for ESC mitigation (range of 10^6 to 10^{10} ohms/square). The surface resistivities for the spray-coated films (P8-P10) were comparable to those obtained for the films containing the SWNT dispersed throughout the matrix (P6 and P7). As expected, the spray-coated films were conductive on only one surface with the opposite surface being insulative ($>10^{12}$ ohms/square). Although the SWNTs were dispersed throughout the matrix in P5, the loading level was not sufficient enough to achieve the percolation threshold needed for conductivity. Film P3 exhibited the lowest surface resistivity of $10^5 \Omega/\text{square}$. However, a tradeoff in properties occurs as this sample exhibited a higher α value and a lower percent transmission at 500 nm as compared to P2.

Table 3. Surface Resistivity Characterization

ID	Description	Surface Resistivity, Ω/square
P1	LaRC TM CP2	$>10^{12}$
P2	SWNT Spray-Coated LaRC TM CP2	10^8
P3	SWNT Spray-Coated LaRC TM CP2	10^5
P4	ASTAA LaRC TM CP2	$>10^{12}$
P5	ASTAA LaRC TM CP2 with 0.03 % (w/w) SWNT	$>10^{11}$
P6	ASTAA LaRC TM CP2 with 0.05 % (w/w) SWNT	1.7×10^7
P7	ASTAA LaRC TM CP2 with 0.08 % (w/w) SWNT	9.2×10^6
P8	SWNT Spray-Coated ASTAA LaRC TM CP2	10^7
P9	SWNT Spray-Coated ASTAA LaRC TM CP2	10^8
P10	SWNT Spray-Coated ASTAA LaRC TM CP2	10^7

3.6 Film Toughness Transparent, conductive film coatings commonly used on spacecraft such as indium tin oxide are extremely brittle and cannot tolerate folding or bending. In order to assess the robustness of the SWNT spray-coated surface, qualitative handling tests were performed. These tests included creasing, folding and crumpling a spray-coated CP2 film and measuring surface resistance after each manipulation. In a separate test, scotch tape was applied to the spray-coated surface and removed, and this was repeated several times. In all of these qualitative tests, the surface resistivity of $10^8 \Omega/\text{square}$ did not change. Such tests applied to an indium tin oxide coated film would likely have resulted in loss of conductivity due to fracture of the coating. These tests indicate that the application of a SWNT dispersion by spray-coating is a viable method to fabricate transparent, conductive, flexible coatings for films.

4. SUMMARY

Films with surface resistivities sufficient to mitigate ESC (10^6 to 10^{10} ohms/square) were prepared by spray-coating one surface of low color polyimides (LaRC™ CP2 and LaRC™ CP2 end-capped with alkoxysilane functional groups) with a suspension of SWNTs in DMF. The surface resistivity and thermo-optical properties of the spray-coated films were compared to films containing SWNTs mixed throughout the bulk of the film at various concentrations. Films containing SWNTs throughout the bulk of the film had volume resistivities sufficient for ESC mitigation but the optical transmission was decreased while the α was increased. In general, it was found that films that were spray-coated with SWNTs exhibited surface resistivities low enough for ESC mitigation with little degradation in the optical transmission and α . A film spray-coated with a SWNT/DMF dispersion exhibited a high degree of flexibility and robustness as evidenced by retention of surface resistance after harsh manipulation.

The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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6. BIOGRAPHIES

Kent A. Watson is a staff scientist with the National Institute of Aerospace (NIA) working in the Advanced Materials and Processing Branch of the Structures and Materials Competency at NASA Langley Research Center (LaRC), Hampton, Virginia. He received a B.S. degree from Oregon State University in 1992 and a Ph.D. from Virginia Commonwealth University in 1998. Prior to joining the NIA, he was a staff scientist with ICASE working at NASA LaRC. His work has focused on the development of space environmentally durable polymers.

Joseph G. Smith, Jr. is a senior polymer scientist in the Advanced Materials and Processing Branch (AMPB) of the Structures and Materials Competency (SMC) at NASA Langley Research Center (LaRC). He received a B.S. degree from High Point College in 1985 and a Ph.D. from Virginia Commonwealth University in 1990. Prior to joining NASA LaRC in September 1994, he held postdoctoral research positions with the University of Akron and Virginia Commonwealth University. His work at NASA has focused on the development of high performance polymers for aerospace applications.

John W. Connell is a senior polymer scientist in the AMPB of the SMC at NASA LaRC. He received B.S. and Ph.D. degrees from Virginia Commonwealth University in 1982 and 1986, respectively. Prior to joining NASA LaRC in January 1988, he was a research associate at Virginia Commonwealth University. Since coming to NASA, his work has focused on the development of high performance polymers for aerospace applications.